

SCIENCE FOR CERAMIC PRODUCTION

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EVOLUTION OF STRUCTURE IN SINTERING CERAMICS BASED ON ALUMINUM OXIDE WITH A EUTECTIC ADDITIVE

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The aspects of sintering of corundum-based ceramics with a eutectic additive of the $\text{MnO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system are considered in the context of the evolution of its structure. In sintering in the presence of a small quantity of eutectic, the behavior of the system is largely different before and after the emergence of the liquid phase. Before the liquid phase formation, the process is determined by the properties of the material located at the site of contact between the particles, and afterwards the system becomes sensitive to the state of the surface of the contact between the solid phase and the eutectic liquid. The latter is due to the fact that the eutectic composition is virtually saturated with respect to aluminum oxide.

Decreasing the sintering temperature of ceramics while preserving a high level of service properties is a topical problem. Additives of a eutectic composition proved to be effective in sintering of corundum ceramics, since they made it possible to bring the sintering temperature down to 1350 – 1450°C and to obtain dense samples in firing in air in furnaces with silicon carbide heaters [1, 2].

An ensemble of particles in a sintered sample is called “an active medium” in synergism. The behavior of a system of particles in sintering involves a modification of the structure of the molded sample. The structure of this sample keeps changing and passes via a succession of stable and unstable states [3]. An input of energy to an open system, namely, a molded piece under heating, is accompanied by the creation of corresponding structures (self-organization) for dissipation or accumulation of energy [4] and largely depends on the degree of nonequilibrium of the process.

Multistability with stable states that significantly differ in their properties is the reason for poor reproducibility of properties in the finished products [5]. Systems in an unstable state have increased sensitivity to various factors. It is possible to make the evolution of a system more predictable by controlling the system in an unstable state by means of internal or external controlling signals, the role of the internal signals being played by the structural elements developed inside the sample in the preceding technological stages [3]. The unstable states that have a determining effect on the sub-

sequent evolution of ceramic structure are termed the principal unstable states. In this context, the objective of a technologist is to identify the principal unstable states and to influence the sintered piece within such a state by external or internal controlling effects in order to ensure the evolution of ceramics in a desired direction [6].

In firing molded pieces made of highly disperse oxide powders, local compaction areas, i.e., denser parts of the molded article, are observed [7]. They are formed in the stages of molding, drying, and sintering. This is a manifestation of cooperative behavior of an ensemble of powder particles (self-organization), which makes it possible to more efficiently dissipate the input energy into the ambient medium or to accumulate it inside the article. The local compaction areas join each other and form a skeleton that penetrates the article and to a large extent determines its strength properties. The development of the skeleton enables the system already in the initial stage of condensation to dissipate energy via the punches and the mold walls. The less compact areas are contained inside the skeleton cavities between the structural elements comprising the skeleton.

The merging of local compactations into a skeleton can be regarded as the formation of a new macrostructural element, as a consequence of the cooperative behavior of these compaction areas. The system strives to create an infinite cluster penetrating the whole sample. After that the skeleton becomes reinforced at the expense of the formation of new force elements participating in energy dissipation toward the punches and the mold walls. The higher the degree of non-

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equilibrium of the process, the sooner the system creates a skeleton and the more cavities it has.

The skeleton has a fractal structure and can be described in the language of the fractal geometry [6]. In this case the molding process represents a progressive formation and destruction of skeletons, which is accompanied by decreasing their cavities and modifying the fractal dimensionality.

It was supposed in [4] that the evolution of the structure of a molded piece in solid-phase sintering of pure oxide ceramics passes via three temperature ranges of the principal unstable states: the first state is related to the evolution of local compactions and correlates with the leveling of the sample fracture (it is observed within the temperature range of 1050–1200°C and has virtually no shrinkage), the second exhibits the maximum shrinkage rate (an inflection in the shrinkage curve), and the third correlates with the disappearance of the infinite cluster of open pores, as they transform into sealed pores. The transition via the third unstable state is related to the beginning of fast growth of the crystals.

The presence of a eutectic additive and a liquid phase makes a determining contribution to the evolution of the ceramic structure. At the same time, before the emergence of the liquid phase (melting of the additive), the evolution of the structure should not be significantly different from the evolution observed in solid-phase sintering.

The purpose of our study was to investigate the sintering process in corundum ceramics with additives of 20% ZrO₂ (here and elsewhere weight content, unless otherwise specified) and a eutectic additive of the MnO–Al₂O₃–SiO₂ system from the point of view of its structural evolution.

The samples were molded from Al₂O₃ powders prepared by different methods. Alumina of grade GLMK (Al₂O₃ with 0.25% MgO) was milled in water by corundum balls in a ball mill for 24 h (GLMK-1) and for 48 h (GLMK-2). The industrial aluminum hydroxide powder was subjected to wet milling by corundum balls in a ball mill for 24 h, with addition of magnesium salt into the mill in the amount converted to 0.25% MgO with respect to Al₂O₃. The suspension was dried, calcined at a temperature of 1350°C, and again milled in the same conditions as before the calcination (Al₂O₃-G). Aluminum hydroxide was produced by spraying aluminum chloride solution into ammonia solution. The precipitate was milled for 3 h in water (Al₂O₃-X-1) or acetone (Al₂O₃-X-2) in a vibration mill with addition of magnesium salt (0.25% MgO with respect to Al₂O₃). The powder was calcined at 1300°C and again milled in the same conditions as before the calcination.

The solution of aluminum chloride and zirconium oxychloride was sprayed into ammonia solution in a ratio corresponding to the eutectic in the Al₂O₃–ZrO₂ system. The precipitate was milled for 3 h in water or acetone in a vibration mill with addition of magnesium salt and yttrium chloride (3 mol.% Y₂O₃ with respect to ZrO₂) and calcined at 1400°C.

The tetragonal ZrO₂ powder was prepared by spraying zirconium oxychloride in ammonia solution with subsequent

milling of the precipitate in an yttrium salt solution (3 mol.% Y₂O₃ with respect to ZrO₂) and calcination at 600°C.

A eutectic additive in the amount of 4% was introduced into the powders. Aluminum and zirconium oxides were mixed with the eutectic sintering additive in an aqueous medium in a vibration mill.

Polyvinyl alcohol was introduced as a temporary technological binder, and samples were molded by bilateral compression at a pressure of 50, 100, and 200 MPa and also hydrostatically at the pressure of 400 MPa. The samples were fired in air within the temperature interval of 1100–1500°C with exposure at the final temperature up to 5 h; the rate of temperature rise was 3 K/min.

The kinetics of sintering in the samples was studied using the nonisothermal sintering method [8]. The formal shrinkage kinetic equation was used for analysis:

$$\frac{dz}{d\tau} = zk_0 \exp\left(-\frac{E}{RT}\right) \frac{E}{RT^2},$$

where $z = 1 - \frac{\Delta l / l_0}{(\Delta l / l_0)_{\max}}$; $\Delta l / l_0$ is the linear shrinkage of

the sample; $(\Delta l / l_0)_{\max}$ is the linear shrinkage of the sample at the maximum firing temperature; τ is the time; k_0 is the multiplicative coefficient; E is the sintering activation energy; R is the universal gas constant; T is the absolute temperature.

After integrating we obtain

$$\ln(-\ln z) = \ln\left(-\frac{k_0}{v}\right) - \frac{E}{RT},$$

where v is the rate of the temperature rise.

The dilatometric sintering curves of the samples with 20% tetragonal ZrO₂ are shown in Fig. 1. Figure 2 shows an example of determining the activation energy for the samples represented in Fig. 1. It can be seen in Fig. 2 that an inflection in the curves is registered at 1100–1150°C. The lines for samples 1 and 2 are virtually parallel under both low and high temperatures, i.e., the sintering activation energy in these cases is virtually equal. The activation energy for sample 3 is significantly higher at low temperatures (before the curve inflection), and afterwards does not differ from the activation energy of samples 1 and 2.

The following explanation can be proposed to account for this course of the curves. A skeleton emerges in molding. An increase in the molding pressure from 50 to 100 MPa results in a significant condensation of the sample (the sample density changes from 1.85 to 2.00 g/cm³). The skeleton structure evidently changes, but the structural elements comprising this skeleton (the local compactions) change to a significantly lesser extent. This is especially true of the particles integrating the local compactions. Their structure changes very little compared with the initial powder. This is the reason for the virtually equal activation energy.

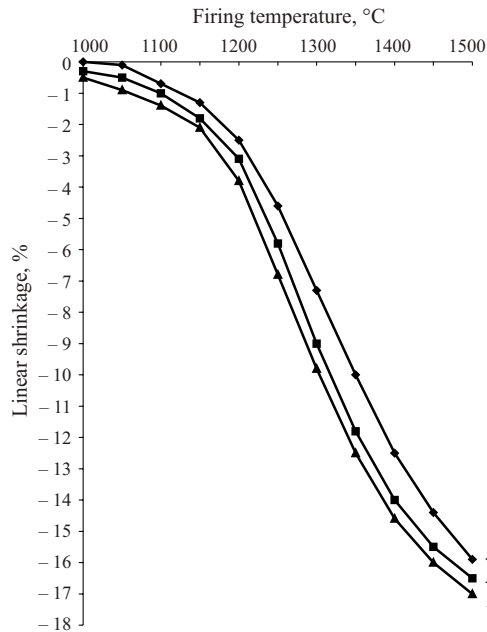


Fig. 1. Dilatometric sintering curves for samples based on $\text{Al}_2\text{O}_3\text{-G}$ + 20% tetragonal ZrO_2 + 4% $\text{MnO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ additive at molding pressure of 50 (1), 100 (2), and 400 (3) MPa.

At a low temperature, the diffusion route passes via the eutectic additive. The main source of vacancies is also located in this additive. The properties of this material, through which the diffusion routes passes, determine the sintering activation energy. The latter agrees with the fact that at low temperatures the activation energy does not depend on the quantity of the additive (while its composition is constant) and the type of the initial aluminum oxide material (Table 1).

The situation in a sample molded at 400 MPa is different. As the molding pressure grows from 100 to 400 MPa, the sample density does not grow as significantly as in going from 50 to 100 MPa (the increased molding pressure produces an increase in the sample density from 2.00 to 2.08 g/cm³). The input mechanical energy partly becomes dissipated in the deformation of the mold walls and partly is accumulated inside the sample. The major part of the energy is consumed in the deformation of the structural elements comprising a strong skeleton. Since the cross-section of a skeleton element is significantly smaller than the cross-section of the sample, the pressure exerted on these structural elements strongly increases.

Significant changes occur to the particles in such conditions. The surface layers of the powdered particles are probably deformed, which squeezes the eutectic additive out from the contact sites, which is primarily observed in the strongest elements of the skeleton that determine the deformation properties of the sample at relatively low temperatures (before the curve inflection in Fig. 1). The contact sites are forced to accumulate a substantial amount of structural defects of the substructural level [9]. At low temperatures (before the curve inflection) the diffusion route in these samples

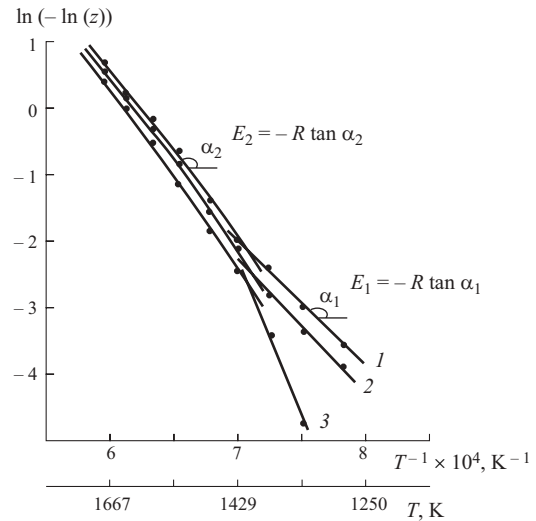


Fig. 2. Example of determining sintering activation energy for ceramic samples. Same designations as in Fig. 1.

mainly passes through corundum and not through the eutectic composition. A great quantity of energy accumulated in the form of structural defects results in the fact that the structure of the corundum contacts rapidly becomes perfected (even before the shrinking of the sample starts). This causes a sharp increase in the process activation energy. The deformation of sample 3 starts as well at a higher temperature.

In the melting of the eutectic, the situation is quite different. The melt composition continuously changes due to the dissolution of corundum and zirconium in this melt. A large surface area of contact, a small quantity of eutectic additive, and a relatively slow heating process causes the melt composition to become nearly saturated with respect to aluminum oxide. The independence of the activation energy from the presence or absence of zirconium dioxide additive indicates that the slowest stage is the mass transfer of aluminum cations. Zirconium cations migrate faster and do not limit the process. In sample 3, the liquid of the eutectic composition after melting rapidly penetrates the contact areas between the particles contained in the strongest elements of the skeleton and starts determining the process activation energy. After the curve inflection, the activation energy of the samples molded at different pressures virtually does not differ. In this case the activation energy is determined by the eutectic melt properties, which turn out to be similar in all samples.

The migration of aluminum cations via the liquid phase consists of several stages: transition from the solid stage into liquid (dissolution); diffusion via the diffusion layer formed on the surface of the solid phase, diffusion in the liquid phase, transfer over the diffusion layer, transition from the liquid phase into the solid phase (crystallization).

To identify the slowest stage, samples of different aluminum oxide materials with a different additive content (2 – 5%) were prepared. The results of measurements of the

TABLE 1

Semidry molding pres- sure, MPa	Amount of additive, %		Activation energy, kJ/mole	
	strengthening	sintering	E_1	E_2
<i>Ceramics based on Al_2O_3-G</i>				
50	20	4	155	208
100	20	4	186	233
400*	20	4	358	236
50	20	1	150	201
50	20	2	160	244
50	20	3	144	210
50	20	5	150	205
200	30	4	215	268
<i>Ceramics based on GLMK-1</i>				
200	20	4	210	416
200	20	4	202	416
<i>Ceramic based on GN-1</i>				
200	20	4	220	450

* Hydrostatic pressing.

activation energy are listed in Table 1. It can be seen that the quantity of the additive does not have a significant effect on the magnitude of E_1 . At the same time, after a liquid phase is formed, the previous history of the material has a perceptible effect on its activation energy. Samples of Al_2O_3 -G have close levels of the activation energy after the inflection of the curves (E_2). This suggests that the main stage is either the transition from the solid phase into a liquid (dissolution) or diffusion through the diffusion layer. At high temperatures most processes are limited by mass transfer via the diffusion layer [10]. A diffusion layer formed on the surface of the dissolving material decreases the effect of the state of this surface on the dissolution rate. In this case the impurities diffusing to the surface (if their content does not exceed certain limits) do not affect the dissolution rate either. However, if the composition of the liquid is saturated with respect to the dissolving material, the concept of the diffusion layer loses its meaning, as its composition and properties virtually do not differ from the properties of the rest of the liquid [10]. In these conditions the system again acquires sensitivity to the state of the surface of the dissolving solid. The actually measured value in this case is the activation energy of the diffusion of aluminum cations via the solid-liquid interface.

It is interesting that the values E_2 (Table 1) in samples based on GLMK-1, GLMK-2, and especially GN-1 powders are close to the activation energy of the volume diffusion of the aluminum cation in corundum (475 kJ/mole) [11]. This suggests that the mass transfer from the solid phase into the liquid of a eutectic composition is largely determined by the velocity of the volume diffusion of vacancies from the near-surface zones of the crystal to the solid-liquid boundary. The process of perfecting the crystalline structure of the material (through which the diffusion flow passes) in the solid-phase sintering of ceramic made of simple oxides proceeds in the similar way [4]. Possibly this is the reason for the fact that

deformation under firing in the presence of a small quantity of eutectic additives does not modify the shape of the samples.

In the course of vacancy removal of defects from the near-surface zones of the crystals, their crystalline structure is perfected, which is clearly demonstrated in Ya. E. Geguzin's work using the example of the formation of a pore-free layer along the crystal boundaries [12]. The perfecting of the crystalline structure of the near-surface zone of the crystals, through which the diffusion path passes, impedes the diffusion mass transfer via these crystals, i.e., delays the mass transfer via the solid – liquid interface. A decrease in the concentration of nonstoichiometric oxygen vacancies causes the mass transfer of oxygen to gradually become less intense than the mass transfer of the cations. In addition, there is diffusion of impurities toward the surface and the purification of the near-surface layer from these impurities. In fact the system itself develops a layer with properties approaching a pure monocrystal in the ceramic crystals. The process of migration of vacancies to the crystal boundaries is still determined by the volume diffusion, but the activation energy of this process increases, and the diffusion velocity decreases and approaches the diffusion velocity of pure monocrystals. These processes are manifested in long-time aging of ceramics and in high-temperature creep.

Under sintering in the presence of a small quantity of eutectics, the behavior of the system (a sintering sample) significantly differs before and after the emergence of the liquid phase. Before the emergence of the liquid phase, the process is determined by the properties of the material located at the site of contact between the particles. Such material under a low molding pressure (up to 100 MPa) is the eutectic additive. Therefore, the activation energy is insensitive to the pre-history of the corundum powder, to which the additive has been added.

Under a high molding pressure (400 MPa), the activation energy of the same material before the formation of the liquid phase is significantly higher, which can be attributed to the eutectic additive being squeezed out from the sites of contact of the powder particles in the strongest areas of the forming skeleton.

After the emergence of the liquid phase, the sensitivity to the molding pressure disappears, since the liquid phase soon dissolves the particle contact sites and penetrates between the particles. Within this range, the activation energy is sensitive to the state of the surface of the solid phase – eutectic liquid contact. This can be accounted for by the fact that the eutectic composition is virtually saturated with respect to aluminum oxide.

The formation of the liquid phase modifies the mass transfer process. The low quantity and the eutectic composition of the liquid phase results in its fast saturation with respect to aluminum oxide. In these conditions the dissolution process is sensitive to the state of the solid – liquid interface surface, and the sintering activation energy becomes increasingly dependent on the previous history of the powder in the

series of Al_2O_3 -G, GLMK, and GN-1, whereas the activation energy in the latter case approaches the activation energy of self-diffusion of aluminum cations in corundum.

Thus the presence of a small quantity of eutectic has a determining effect on the evolution of the ceramic structure. Prior to the formation of the liquid phase, the process depends on the properties of the material located in the contact zones between the particles, and after that a determining factor is the state of the surface of the solid phase – eutectic liquid contact, when this liquid approaches the level of saturation with aluminum oxide.

REFERENCES

1. E. S. Lukin, N. T. Andrianov, N. B. Mamaeva, et al., "The problem of producing oxide ceramics with a controlled structure," *Ogneupory*, No. 5, 11 – 15 (1993).
2. E. S. Lukin and N. A. Makarov, "Specifics of selecting additives in technology of corundum ceramics with a decreased sintering temperature," *Ogneup. Tekh. Keram.*, No. 9, 10 – 15 (1999).
3. V. S. Bakunov and A. V. Belyakov, "Prospects for improving reproducibility of the structure and properties of ceramics," *Ogneup. Tekh. Keram.*, No. 2, 16 – 21 (1998).
4. A. V. Belyakov, "Main bifurcations in firing dense oxide ceramics," *Steklo Keram.*, No. 10, 8 – 14 (2000).
5. A. Yu. Loskutov, "Reproducibility of the structure and properties of articles and their description in the context of nonlinear dynamics," *Steklo Keram.*, No. 7, 12 – 16 (2000).
6. V. S. Ivanova, A. S. Balankin, I. Zh. Bunin, et al., *Synergism and Fractals in Science of Materials* [in Russian], Nauka, Moscow (1994).
7. A. V. Belyakov and A. S. En'ko, "A study of fractures of molded pieces with tinted granules to identify local compactions," *Steklo Keram.*, No. 12, 19 – 22 (1999).
8. K. K. Strelov and I. D. Kashcheev, *Theoretical Principles of Refractory Materials Technology* [in Russian], Metallurgiya, Moscow (1996).
9. V. S. Bakunov and A. V. Belyakov, "The problem of analysis of the structure of ceramics," *Neorg. Mater.*, **32**(2), 243 – 248 (1996).
10. A. V. Belyakov, *Chemical Resistance of Ceramics* [in Russian], Izd-vo MKhTI, Moscow (1982).
11. A. E. Paliachino and W. D. Kingery, "Aluminium ion diffusion in aluminium oxide," *J. Chem. Phys.*, **37**(5), 957 – 962 (1962).
12. Ya. E. Geguzin, *Physics of Sintering* [Russian translation], Nauka, Moscow (1967).